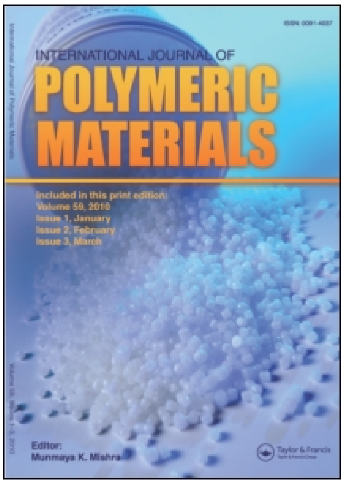

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Cárdenás T. Galo[a]; González G. Marcela[a]
[a] Departamento de Polímeros, Facultad de Ciencias Químicas, Universidad de Concepción, Concepción, Chile

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Thermal Analysis of Metal Poly(Styrene-*co*-Butylmethacrylate) Part XVII

GALO CÁRDENÁS T.* and MARCELA GONZÁLEZ G.

Departamento de Polímeros, Facultad de Ciencias Químicas,
Universidad de Concepción, Casilla 3-C, Concepción, Chile

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Metal poly(styrene-co-butylmethacrylate)s copolymers were obtained by radical copolymerization with benzoyl peroxide (BPO). The monomers were cocondensed with several metals: Pd, Au, Cu, Ag, In, Ge, Ga, Sn, Sb, Zn, Cd and Bi at 77K. After the warming process, metal comonomer colloids can be obtained. The colloids were polymerized with BPO at 65°C for 3 h. The thermal stabilities of these metals have been studied by thermogravimetry between 25 and 550°C under nitrogen flow. The decomposition temperature was obtained from the maximum of the first derivative from TG curve. The kinetic parameters of the thermal decomposition were determined by the Arrhenius equation. All these copolymers degrade in one stage. The kinetic data thus obtained show the thermostabilities decrease in the order: Ga-SBMA > Ag-SBMA > Au-SBMA > In-SBMA > Ge-SBMA > Zn-SBMA > Sn-SBMA > Bi-SBMA > Cd-SBMA > Pd-SBMA > Cu-SBMA > Sb-SBMA. The thermal stability is strongly related to the metal cluster incorporated in the copolymers. The decomposition reaction order is zero in all the copolymers. The pre-exponential factor, the activation energy, the reaction order and the decomposition temperature for all the metal copolymers have been determined.

Keywords: Poly(styrene-*co*-butylmethacrylate); metal clusters; thermal analysis; thermal stability; activation energy

INTRODUCTION

The degradation of polymers involves a wide range of chemical and physical processes ending with simple products. These are low molecular organic compounds, carbon dioxide and water.

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*Author to whom correspondence should be addressed.

There are several methods for the preparation of polymer-metal composites and they are generally focused on plasma polymer then films including simultaneous- plasma etching and plasma polymerization [1,2], simultaneous evaporation of polymers and metal from separate sources or simultaneous plasma polymerization [3–9].

In other experiments, metal ions were generated by pulsed-laser vaporization of a metal target placed above the monomer liquid inside a vaccum chamber [6]. Ti, Zr and Sn have been used to obtain polyisobutylene ranging from $\overline{M}_n = 5.5 \times 10^5$ to $\overline{M}_n = 1 \times 10^6$.

Polymerization reactions have also been observed following the reactions of transition metal cations with olefinic molecules both in the gas phase [7,8] and in clusters [9].

More recently, the polymerization of isobutylene clusters initiated by Al^{+3} in the presence of small concentration of $(CH_3)_3CCl$.

In the present study, we investigate the thermal stability of poly(styrene-*co*-butylmethacrylate) doped with several metal clusters. During the cocondensation metal atoms are generated. Our studies are focused to establish a relation between the metal presence in the copolymers and their thermal stability and changes in kinetic parameters.

EXPERIMENTAL

Colloid Synthesis

The colloids metal (styrene-*co*-butylmethacrylate)s were prepared by cocondensation of the monomers with the metals at 77 K using a metal atom reactor [11,12]. Two concentrations of metal dispersed in the monomers were used. Different current intensities were used depending upon the metal used and the vacuum.

Typical Copolymerization

As a typical copolymerization, Gallium colloid (10 mL) was placed in a polymerization flask with 1.0 mol % of benzoyl peroxide (BPO) under nitrogen atmosphere. The flask was closed and placed in an isothermal bath at 65°C for 3.0 h. The content of each flask was poured in 100 ml of methanol. The black copolymer was filtered off and dried under vacuum (10^{-2} Torr) for 48 h at 40°C. The yield of the copolymer was determined. Similar procedure was followed for 1.5, 3.0 and 5.0 mol % BPO.

Molecular Weights

The viscosimetric molecular weights ($\bar{M}$v) were determined by using an Ostwald viscometer. The samples were dissolved in 2-butanone at 25°C and the parameters $K = 5.3 \times 10^{-3}$ ml/g; $a = 0.76$ were used [13].

Thermogravimetry

A Perkin-Elmer Model TGS-2 Thermogravimetric System, with a microprocessor driven temperature control unit and a TA data station, was used. The mass of the samples was generally in the range of 2–4 mg. The sample pan was placed in the balance system in equipment and the temperature was raised from 25 to 550°C at a heating rate of 10°C/min. The mass of the sample pan was continuously recorded as a function of the temperature.

Elemental Analysis

A Perkin-Elmer 2100 Automatic Analyzer for C/H determination was used. The metals in a Perkin-Elmer 3500 Atomic Absorption were determined.

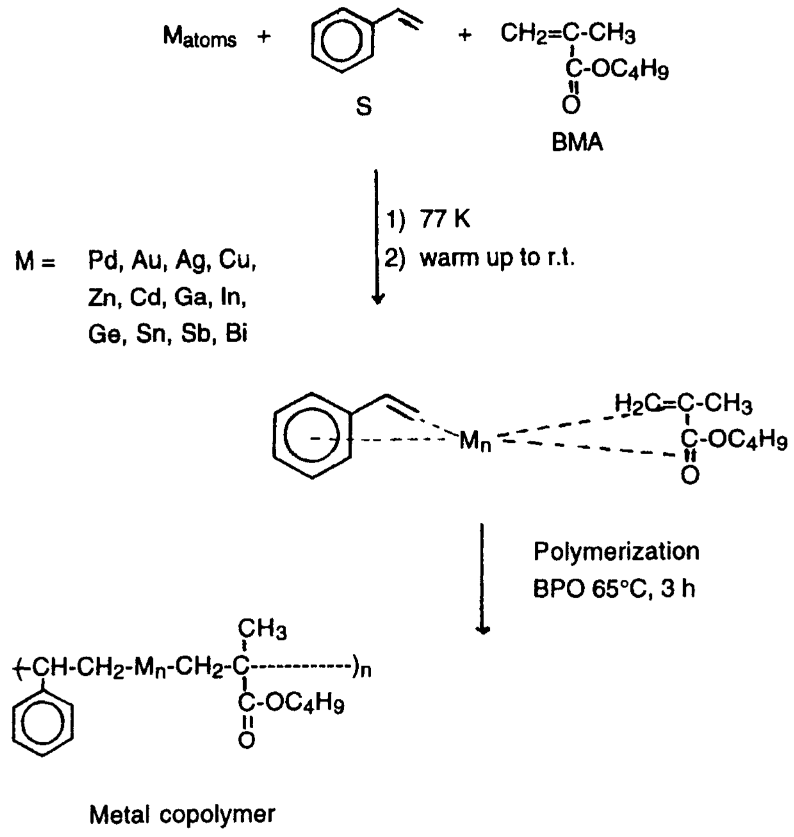
RESULTS AND DISCUSSION

The synthesis of metal poly(styrene-*co*-butylmethacrylate) copolymers with BPO has been already reported [14]. The copolymers exhibited a low metal content and they can be prepared by cocondensation of the metal and the monomers at 77 K. The synthesis is shown in the following scheme:

All the copolymers showed a low level of metal cluster incorporation, Ge being the lowest 0.10, and Cu the highest 3.20%. The presence of metal clusters in the copolymers are increasing the thermal stability of the undoped analogues. Ge and Sn-SBMA exhibited a high metal cluster content and also they exhibited higher stabilities.

The molecular weights ($\bar{M}v$) of these copolymers range between 2.4×10^3 and 1.5×10^5 g/mol. Stable metals such as Au and Ag showed similar T_D, being higher than the one corresponding to the higher MW fractions. Cu, Sb and Bi-SBMA behaves different due to their facility for oxidation even at very low oxygen presence.

In Figure 1 we have summarized thermograms of the four fraction of $\bar{M}_v$ corresponding to the undoped copolymer. We have found that in all the



Scheme

polymers and copolymers the higher the molecular weight, the higher the decomposition temperature [15,16,17]. The thermal decomposition temperatures (T_D) are quite different 355 for Cu-SBMA and 418°C for Ga-SBMA. Almost, in all the cases (Bi, Zn, Sn are exceptions) the fractions of higher MW show the higher stability.

For polymer degradation, the thermal decomposition kinetics of the thermogravimetric weight loss data were assumed to the kinetic equation,

$$-(d\alpha/dt) = k(1-\alpha)^n \tag{1}$$

where α is the fraction of the sample weight reacted at time t, and k is the rate constant where n is the order of reaction. The reaction rates, $d\alpha/dt$, were calculated using a differential technique with the heating rate (10°C

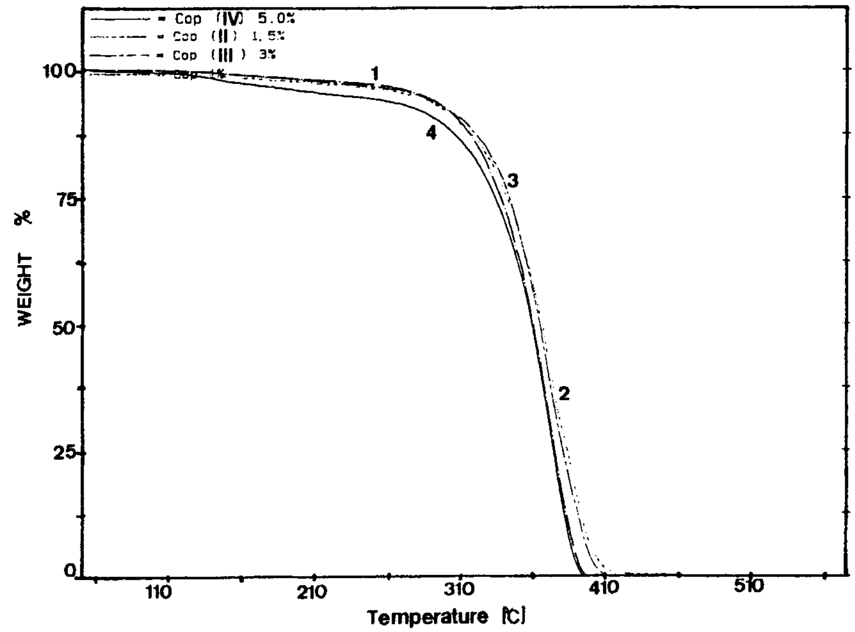


FIGURE 1 Thermogram of poly (styrene-*co*-butylmethacrylate) copolymers obtained by heating the polymers from 25 to 550°C at 10°C min^{-1}. $1 = 1.0$, $2 = 1.5$; $3 = 3.0$ and $4 = 5.0$ mol%.

min^{-1}) incorporated directly in the data of temperature versus sample weight fraction, according to the method developed by Wen and Lin [18]. The Arrhenius equation is the model generally used to express the temperature-dependence of rates of reaction:

$$k(T) = A\exp(-E/RT) \tag{2}$$

where R is gas constant, A is the pre-exponentail factor, and E is the activation energy. After combining equations (1) and (2) and using the logarithmic form we obtained:

$$\beta = \ln[-d\alpha/dT)/6(1-\alpha)^n] = \ln A = E/RT \tag{3}$$

A computer linear multiple-regression program was used to calculate the kinetic parameters E and A linear least-squares fit of the data in a semilogarithmic plot of β versus $1/T$.

Mass loss experiments measure processes which are heterogeneous by definition and which are complicated by chemical and physical processes taking place in the condensed phase [19].

For copolymers, the degradation processes consist of several steps, each with its proper set of kinetic parameters, so we can assume that identical or average values are sufficient to represent the overall process.

Figure 2 showed the thermogram and first derivative of Ga- poly(styrene-*co*-butylmethacrylate)s. On Figure 2a the higher M_n fraction showed a T_D at

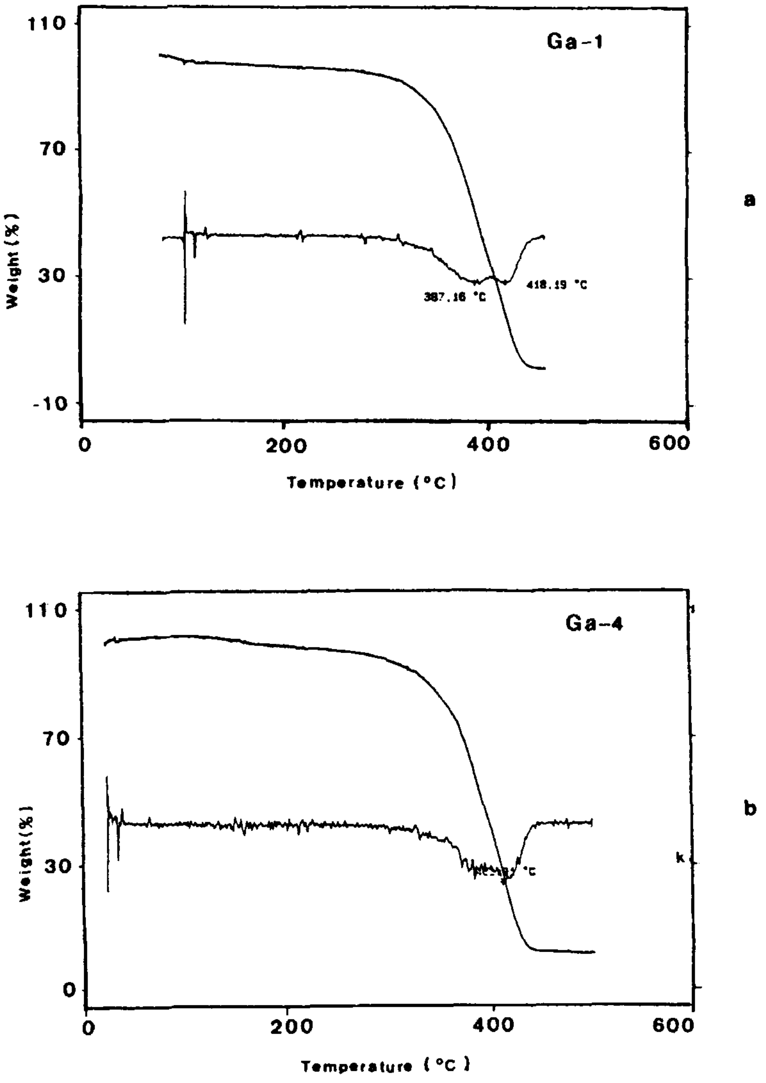


FIGURE 2 Thermogram and first derivative of Ga poly(styrene-co-buty/methacrylate)s obtained at a heating rate of 10°C min^{-1}. (a) Fraction of 1.0 mol%, (b) fraction of 5.0 mol% BPO, respectively.

418.19°C and Figure 2b, the lower MW fraction showed a T_D at 411.81°C. Those values are over 45°C more stable than the undoped copolymers.

Table I summarized the order of decomposition reaction, the temperature range in which the activation energy (E_a) was calculated, the E_a and the T_D for 2 fractions of each copolymer. The E_a values were found for Pd-SBMA with 44.58 and 29.63 kJ/mol. Also, Ag-SBMA showed a higher T_D at

TABLE I Kinetic parameters for metal poly(styrene-*co*-butylmethacrylate)s copolymers

Copolymer	*n*	*Temp. Range (°C)*	E_a *(kJ/mol)*	T_D *(°C)*
SBMA-1	0	351.60–388.00	42.45	372.18
SBMA-4	0	335.13–394.93	40.76	393.70
Ga-SBMA-1	0	361.36–427.40	36.26	418.19
-4	0	357.56–435.37	38.77	411.81
Ag-SBMA-1	0	361.27–431.48	42.50	391.00
-4	0	336.88–422.96	28.58	383.34
Au-SBMA-1	0	360.26–420.06	40.49	388.79
-4	0	330.36–385.40	41.30	363.73
In-SBMA-1	0	100.93–437.92	40.67	388.52
-4	0	340.95–426.59	27.59	381.10
Ge-SBMA-1	0	356.00–429.45	35.26	387.15
-4	0	343.00–416.74	44.08	384.80
Zn-SBMA-1	0	350.30–400.13	39.76	376.51
-4	0	366.33–416.16	32.72	394.71
Sn-SBMA-1	0	342.93–397-10	35.97	373.05
-4	0	340.33–395.36	36.69	374.78
Bi-SBMA-1	0	325.16–385.40	36.44	366.26
-4	0	320.40–390.16	41.80	378.68
Cd-SBMA-1	0	320.40–395.36	34.25	366.11
-4	0	325.16–395.36	28.82	365.25
Pd-SBMA-1	0	320.83–380.20	44.58	355.50
-4	0	320.40–390.16	29.63	353.55
Cu-SBMA-1	0	345.05–426.80	27.24	353.77
-4	0	359.50–434.87	44.25	353.77

SBMA = poly(styrene-*co*-butylmethacrylate)s.
T_D = decomposition temperature.
1,4 = correspond to fraction of highest and lowest molecular weight.

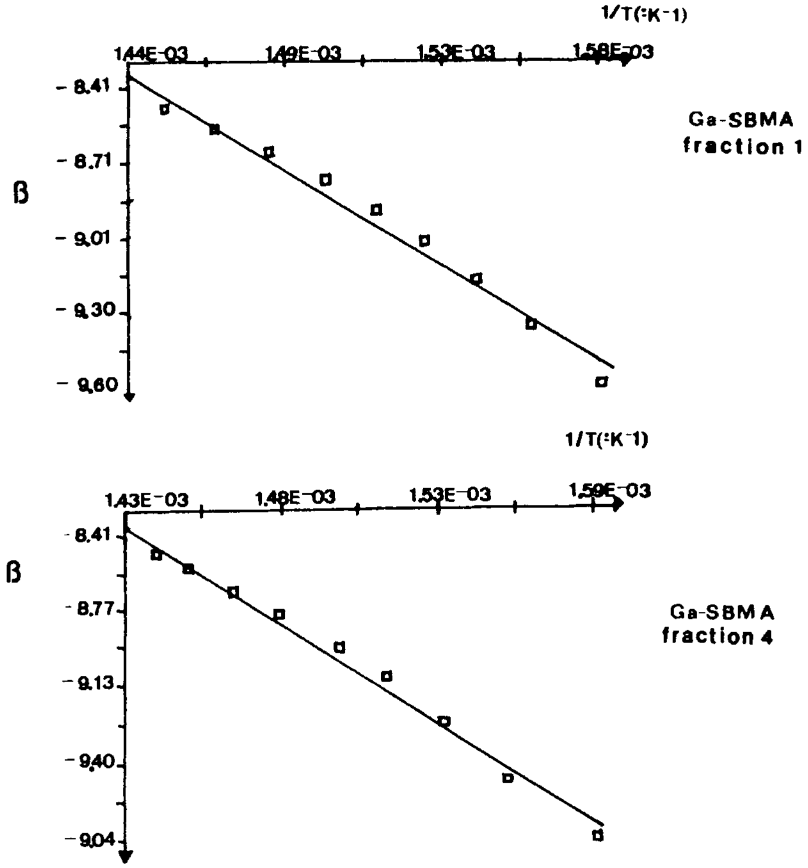


FIGURE 3a Arrehenius plot of Ga-SBMA (fractions 1 and 4) and Ag-SBMA (fractions 1 and 4).

391.0°C and E_a 42.50 kJ/mol. The activation energies of Pd, Ag, Au and In-SBMA are the highest and comparable to the PBMA [22] series previously reported. Cu-SBMA showed the lower T_D most probably to the high oxidation potential. In general, the addition of metal clusters increases the thermal stability for most of the copolymers.

The series of PMMA also exhibited good stability and high E_a for Au doped polymers [15]. In general, stable metals like Pd and Au exhibit the most relevant values in the activation energy of the decomposition reactions.

The metal copolymers S-*co*-MMA already reported [21] also showed high E_a values for Au and Pd copolymers.

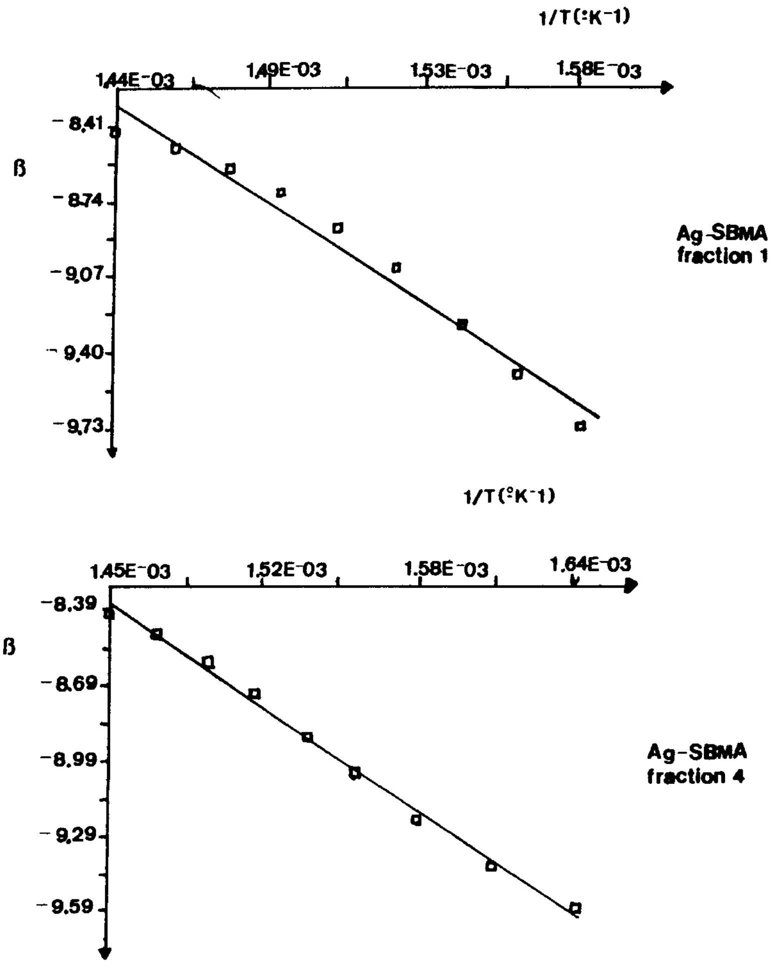


FIGURE 3b

For vinyl polymer degradation, several series of reactions involving homologous species give the same rate constant. Nevertheless, it can be accepted that the values obtained under the known conditions yield a good estimation.

The thermal degradation of these copolymers doped with metal clusters is very useful for analyzing the thermal stability and for determining the temperature range in which they can be used. It is interesting to observe the influence of the metal clusters in the copolymers stability. This is of great importance for successful application of these new materials.

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